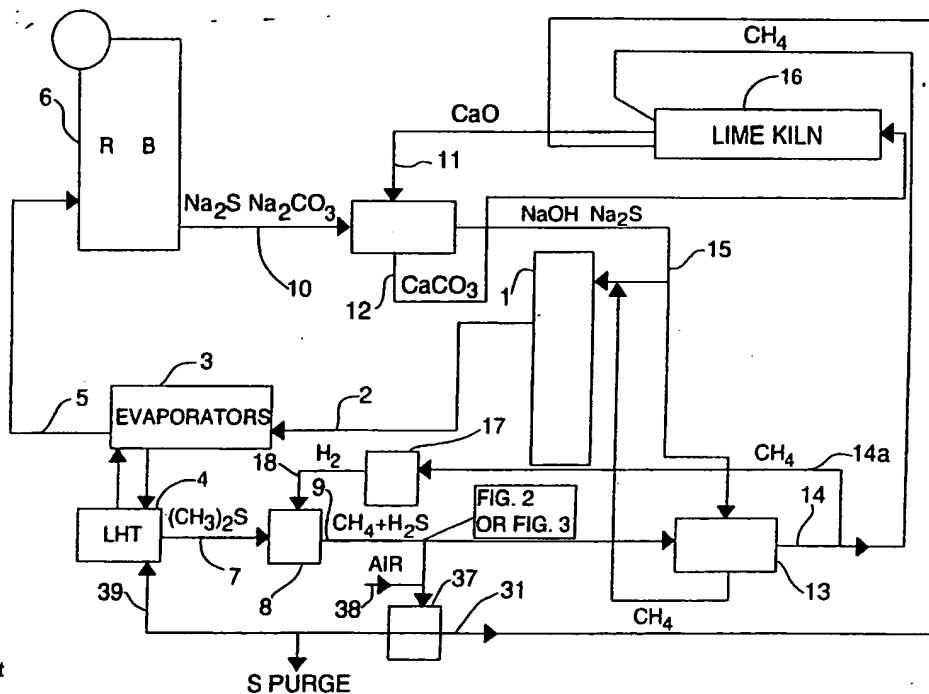




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US92/00924 <b>(22) International Filing Date:</b> 5 February 1992 (05.02.92) <b>(30) Priority data:</b> 651,462 6 February 1991 (06.02.91) US <b>(71) Applicant (for all designated States except US):</b> A. AHLSTROM CORPORATION [FI/FI]; SF-29600 Noor-markku (FI). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> RYHAM, Rolf [SE/US]; 5170 Overbend Trail, Suwanee, GA 30174 (US). <b>(74) Agent:</b> PONTANI, Thomas, C.; Cohen, Pontani, Lieberman & Pavane, 551 Fifth Avenue, New York, NY 10176 (US).		<b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), NO, PL, SE (European patent), US.  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: A METHOD OF RECOVERING ENERGY AND CHEMICALS FROM BLACK LIQUOR



(57) Abstract

A method and apparatus for treating black liquor generated in a sulfate pulping process to recover energy and chemicals therefrom includes heating (4) the black liquor (2) at a temperature and for a time period to produce substantial volumes of off gases (7) containing organic sulfur compounds; generating hydrogen sulfide (9) and preferably methane from the off gases; and utilizing the generated hydrogen sulfide in the sulfate pulping process. The hydrogen sulfide can be absorbed (13) into white liquor (15) to selectively control the sulfur content of the white liquor. The methane (31) is used as fuel in a lime reburning kiln (16).

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1  
2           **A METHOD OF RECOVERING ENERGY AND CHEMICALS FROM**  
3           **BLACK LIQUOR**  
4

5  
6           BACKGROUND AND SUMMARY OF THE INVENTION  
7

8  
9           Wood is treated in sulfate cooking by white liquor  
10          containing NaOH and Na<sub>2</sub>S, whereby lignin is dissolved  
11          and cellulose fibers are released. The mixture of  
12          cellulose fibers (pulp) and cooking chemicals,  
13          mainly containing sodium hydroxide and sodium  
14          sulfide, is treated with water, whereby black  
15          liquor is generated. The black liquor is  
16          concentrated by evaporation. The concentrated black  
17          liquor is combusted in a soda recovery boiler and  
18          the chemical melt thus produced and mainly  
19          containing Na<sub>2</sub>S and Na<sub>2</sub>CO<sub>3</sub> is dissolved in water,  
20          whereby green liquor is generated. The green liquor  
21          is causticized by caustic lime (CaO) to yield white  
22          liquor containing Na<sub>2</sub>S and NaOH. Another product of  
23          the causticizing process is lime sludge mainly  
24          formed by CaCO<sub>3</sub>. White liquor is transferred to a  
25          digester house and the lime sludge is calcinated in  
26          a lime sludge reburning kiln to caustic lime being  
27          reutilized in the causticizing.

28          Sulfur emissions are generated in a sulfate  
29          cellulose mill mainly in the soda recovery boiler,  
30          the evaporation plant and the digester house. In  
31          order to decrease the environmental impact of the  
32          sulfur the emissions thereof should be minimized.

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1           It has been noted that the increase of the dry  
2           solids content of black liquor decreases the sulfur  
3           emissions of a soda recovery boiler. On the other  
4           hand, the sulfur content of green liquor increases  
5           due to the above and thus the sulfidity of white  
6           liquor as well as the sulfur content of the black  
7           liquor are also increased. It can also be assumed  
8           that the sulfur emissions of the evaporation plant  
9           increase due to the higher sulfur content of the  
10          black liquor.

11          Finnish published application 75615 (US Pat. No.  
12          4,929,307) teaches that the viscosity of the black  
13          liquor can be decreased by heat treating the black  
14          liquor at a temperature higher than its cooking  
15          temperature. Due to this it is possible to  
16          evaporate black liquor to a higher dry solids  
17          content, whereby the sulfur emissions of a soda  
18          recovery boiler are decreased.

19          It is appreciated from US Patent 2,711,430 to heat  
20          black liquor to thereby release organic sulfur  
21          compounds.

22          Co-pending US Patent Application Serial No. 614,722  
23          discloses a method for removing sulfur from black  
24          liquor. The black liquor is heated preferably  
25          before the last effect of the evaporation at a  
26          temperature higher than the cooking temperature and  
27          the sulfidity of white liquor is adjusted by  
28          adjusting the temperature and/or retention time of  
29          the heat treatment so that a desired amount of  
30          sulfur compounds, such as organic sulfur compounds,  
31          including mainly dimethyl sulfide and methyl  
32          mercaptan, are separated from the gaseous black

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1           liquor.

2           In the heat treatment of black liquor the long  
3           lignin/saccharide chains are split and the methoxy  
4           groups in the black liquor will form dimethyl  
5           sulfide (DMS) as a byproduct. Approximately 4-6  
6           weight-% of the dry solids of the black liquor can  
7           potentially become gas containing dimethyl sulfide.

8

9           Surprisingly, it has been noted that the  
10          above-mentioned phenomena can be utilized in a  
11          completely new manner.

12

13          According to the present invention, a method is  
14          provided for treatment of black liquor generated in  
15          a sulfate pulping process to recover energy and  
16          chemicals therefrom, in which method

17          (a) the black liquor is heated at a temperature and  
18          for a time period such that substantial volumes of  
19          off gases containing organic sulfur compounds are  
20          produced;

21          (b) generating methane and hydrogen sulfide from at  
22          least a part of the off gases; and

23          (c) utilizing the generated hydrogen sulfide in the  
24          sulfate pulping process.

25          The apparatus according to the present invention  
26          comprises

27          means for heating the black liquor for a period of  
28          time so as to generate off gases containing organic  
29          sulfur compounds;

30          means connected to the heating means for generating  
31          hydrogen sulfide from the organic sulfur compounds  
32          contained in the off gases;

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1 means connected to the hydrogen  
2 sulfide generating means for controlling the  
3 sulfidity of white liquor and for separating the  
4 methane from the hydrogen sulfide by selectively  
5 passing the methane and the hydrogen sulfide into  
6 contact with the white liquor; and

7 means connected to the sulfidity  
8 control means for feeding the white liquor of  
9 controlled sulfidity to the cooking stage of a  
10 sulfate pulping process.

11  
12 The generated hydrogen sulfide can be  
13 separated from the gas stream by absorption in NaOH  
14 solution or in white liquor prior to the cooking  
15 stage. Thus it is possible to increase and control  
16 the sulphidity of white liquor. This is very  
17 advantageous, because a higher sulfide concentration  
18 in white liquor produces kraft pulp with a higher  
19 viscosity and better physical properties.

20 Alternatively, the  $H_2S$  can be absorbed in  
21 an amine absorber or similar device. An alternative  
22 to absorption is separation by compression and  
23 successive partial condensation. The hydrogen  
24 sulfide separated can be used for many purposes, for  
25 instance, it can be converted into elementary sulfur  
26 in a process similar to the Claus process. The  
27 sulfur formed is fed back into the heat treatment  
28 reactor, in which the black liquor is treated, to  
29 enhance the formation of new dimethyl sulfide or the  
30 sulfur is purged from the system as crystalline  
31 sulfur.

32 The produced  $H_2S$  can be used in the pulping

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1 process to considerably improve the pulping yield by  
2 pre-impregnation of  $H_2S$  into the wood-chips before  
3 the alkaline delignification process. Preferably  
4 the off gases are treated in such a way that in  
5 addition to hydrogen sulfide methane is also  
6 produced. The methane produced can be used, for  
7 instance, to substitute the fuel normally used in  
8 the lime reburning operation. A part of the off  
9 gases can, if required, be treated in such a way  
10 that other compounds than hydrogen sulfide are  
11 produced, for example, sulfur dioxide. By means of  
12 the present method the removal of the sulfur from  
13 the black liquor and the recycling of the sulfur in  
14 the kraft liquor recovery process are improved. A  
15 substantial portion of sulfur can bypass the soda  
16 recovery boiler and the sulfur recovered can be  
17 returned to the pulping process, for instance, to  
18 cooking liquors.

19 It is now also possible to partially  
20 convert black liquor to usable fuel, which can be  
21 used in pulping operations, e.g. in lime kilns, or  
22 outside such operations. It can also be used in a  
23 separate superheater of the soda recovery boiler or  
24 in other boilers.

25 When sulfur is separated from black  
26 liquor, in the manner described, before it is  
27 supplied to the soda recovery boiler, the dry solids  
28 flow flowing into the boiler can decrease by about  
29 10% (corresponding to an increase in throughput of  
30 the recovery boiler by about 10%) and, at the same  
31 time, the net heat content of the black liquor is  
32 reduced. In other words, the load of the boiler as

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1 well as the amount of sulfur to be processed are  
2 decreased.

3 By adjusting the temperature and/or  
4 retention time of the heat treatment it is possible  
5 to adjust the amount of the dimethyl sulfide and  
6 other organic sulfur compounds exiting from the  
7 black liquor. The formation of dimethyl sulfide can  
8 be adjusted also by feeding sulfur to the heat  
9 treatment reactor.

10 The heat treatment is carried out as  
11 pressure heating at a temperature of approximately  
12 170-350°C, preferably higher than 190°C, and more  
13 preferably between 190 and 290°C. The treatment  
14 time depends on the temperature and the quality of  
15 the liquor. The retention time is typically about  
16 1-60 minutes in order to generate gas including  
17 sulfur compounds to a significant extent. The  
18 treatment can always be carried out when the removal  
19 of sulfur from black liquor is desired. Preferably,  
20 the treatment is carried out prior to the final  
21 evaporation.

22



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BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described below by way of example with reference to the accompanying drawings, in which:

FIG. 1 is a schematic diagram illustrating the method of improving the utilization of sulfur compounds in the kraft pulping process in accordance with the present invention;

FIG. 2 is a diagram illustrating a method for separating hydrogen sulfide from methane in the method of FIG. 1; and

FIG. 3 is another schematic illustration of yet a further method for separating hydrogen sulfide from methane in the method of FIG. 1.

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1                    DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED  
2                    EMBODIMENTS

3  
4                    In Fig. 1 the weak black liquor is fed  
5                    from a digester house 1 through line 2 to, and is  
6                    evaporated in, for instance, a multiple effect  
7                    evaporating system 3 in accordance with US Patent  
8                    4,953,607 the entire disclosure of which is hereby  
9                    incorporated by reference. The lignin in the liquor  
10                   to be evaporated is split by a heat treatment, that  
11                   is, by heating the black liquor under pressure for  
12                   a predetermined time, in a reactor vessel 4, whereby  
13                   gases containing organic sulfur compounds are  
14                   generated. At temperatures over 200°C the amount of  
15                   sulfur exiting from the black liquor can be 30-65%  
16                   of all sulphur contained in the black liquor. The  
17                   heat treatment is carried out under water pressure,  
18                   i.e. at pressures varying from about 8 bars to 165  
19                   bars, preferably from about 12 bars to 80 bars.  
20                   Suitable temperatures for the heat treatment range  
21                   from about 170-350°C and preferably from 190-290°C.  
22                   At these temperatures substantially all of the  
23                   organic sulfur compounds, which are formed in the  
24                   black liquor during the heat treatment, are  
25                   liberated in form of gas. For example, at a  
26                   temperature of 280°C this gas contains about 65%  
27                   dimethyl sulfide, about 34% methyl mercaptan and 1%  
28                   hydrogen sulfide.

29                   The objective of the pressure heating is,  
30                   on one hand, to decrease the viscosity of the black  
31                   liquor to be concentrated thereby improving the  
32                   evaporation and treatment abilities of the liquor,

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1 and, on the other hand, to remove sulfur therefrom.  
2 The heat treatment causes the splitting of the  
3 lignin in the black liquor, which, in turn, results  
4 in a decrease of the viscosity thereof. At the same  
5 time methoxy groups of lignin split off, thereby  
6 generating dimethyl sulfide (DMS).

7 The concentrated black liquor is  
8 transferred through line 5 to a soda recovery boiler  
9 6 for combustion therein. The chemical melt thus  
10 produced and mainly containing  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{CO}_3$  is  
11 dissolved in water, whereby green liquor in line 10  
12 is generated. The green liquor is thereafter  
13 causticized in a suitable vessel with lime ( $\text{CaO}$ )  
14 added through line 11 to form white liquor exiting  
15 through line 15, and which is transferred to the  
16 digester 1 or for further treatment. The lime mud  
17 also formed during the causticizing step is fed  
18 through line 12 into a lime kiln to be calcined  
19 therein to recover the lime therefrom.

20 Dimethyl sulfide (DMS) formed during the  
21 above described heat treatment of the black liquor  
22 in reactor vessel 4 is fed through line 7 into  
23 hydroconverter 8 and reduced therein to methane and  
24 hydrogen sulfide. This reduction of DMS is achieved  
25 with  $\text{H}_2$  or  $\text{CO} + \text{H}_2$  at a temperature of about  $300^\circ\text{C}$ .  
26  $\text{H}_2\text{S}$  can be separated from the gas mixture ( $\text{CH}_4$  and  
27  $\text{H}_2\text{S}$ ) contained in line 9 by absorption thereof in a  
28 white liquor scrubber 13, whereby a substantially  
29 sulfur-free  $\text{CH}_4$  gas is produced.  $\text{H}_2\text{S}$  reacts with  
30  $\text{NaOH}$  as follows:  $2 \text{CH}_4 + \text{H}_2\text{S} + 2\text{NaOH} \rightarrow \text{Na}_2\text{S} + 2\text{CH}_4$   
31  $+ 2\text{H}_2\text{O}$ .

32 Because sulfur is removed from the black

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1           liquor prior to the soda recovery boiler, the sulfur  
2           content of white liquor produced from this liquor is  
3           lower than that of white liquor normally used in  
4           cooking. The white liquor having low sulfur content  
5           in line 15 can be used in the later stages of  
6           cooking. As mentioned above, a portion of white  
7           liquor is added into scrubber 13 through line 15a,  
8           where it absorbs the sulfur compounds and the sulfur  
9           content thereof increases. Preferably it is then  
10          transferred through line 15b to the upper part of  
11          the digester 1 to increase the sulfidity and thus  
12          improve the pulp yield and pulp quality. A higher  
13          white liquor sulfidity is preferred at the beginning  
14          of cooking than in the later stages. For example,  
15          by maintaining the same viscosity value with the  
16          present method as with conventional method it is  
17          possible to decrease the previously obtained kappa  
18          number by 5.

19                 A portion of the methane gas is fed  
20                 through line 14 to a lime kiln 16 to substitute the  
21                 fuel normally used therein. Another portion of the  
22                 methane is fed through line 14a, after the white  
23                 liquor scrubber, to a converter 17 and is converted  
24                 therein to carbon monoxide and hydrogen through  
25                 sub-stoichiometric combustion, which is a  
26                 conventional method. The hydrogen and carbon  
27                 monoxide 18 are fed to hydroconverter 8 to be used  
28                 therein to reduce the dimethyl sulfide to methane  
29                 and hydrogen sulfide.

30                 Alternatively to absorbing the hydrogen  
31                 sulfide as described, the  $H_2S$  can also be separated  
32                 by compression and partial condensation as

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1 illustrated in Fig. 2. The gas mixture containing  
2 methane and hydrogen sulfide is compressed in a  
3 pressure apparatus 20 to a pressure of at least 20  
4 bar and partially condensed in condenser 21 so that  
5 most of the hydrogen sulfide 22 is separated from  
6 the methane. The produced  $H_2S$  exiting therefrom  
7 through line 22 can be used in the pulping process  
8 to considerably improve the pulping yield by  
9 pre-impregnating the wood-chips with  $H_2S$  before the  
10 alkaline delignification process. The production  
11 increase based on fiber production is at least  
12 10-12%. The remainder of the gas mixture is  
13 transferred through line 12 to an absorber 23 and  
14 absorbed therein using methanol as an absorbent,  
15 thereby separating the remaining hydrogen sulfide  
16 from the methane. The free methane gas in line 25  
17 can then be used in the lime kiln as fuel as  
18 described above.

19 Alternatively the gas mixture containing  
20 methane and hydrogen sulfide after the hydrogen  
21 converter 8 can also be treated by absorption as  
22 follows. The hydrogen sulfide is separated from the  
23 methane by absorbing it into an amine solution  
24 containing methylamine in an amine scrubber 30 as  
25 illustrated in Fig. 3. The methane exiting from the  
26 scrubber is transferred through line 31 to the lime  
27 kiln 16 to be used as a fuel. The amine solution  
28 containing the hydrogen sulfide is transferred  
29 through line 32 to an amine stripper 34, wherein the  
30 hydrogen sulfide is separated by the addition of  
31 steam. The amine solution in line 35 which is free  
32 from  $H_2S$  is fed back to scrubber 30 through a heat

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1           exchanger 33, in which the solution coming from the  
2           scrubber is preheated. The hydrogen sulfide exiting  
3           from the stripper 34 through line 36 can be utilized  
4           as described earlier.

5           Further, a part or the entire flow of  
6           hydrogen sulfide can be oxidized to elementary  
7           sulfur according to processes similar to the Claus  
8           process, such as the method described in US Patent  
9           No. 4,919,914 which is also incorporated herein in  
10          its entirety by reference. Also, the gas mixture in  
11          line 9 after the hydroconverter 8 can be treated by  
12          this method. This method is based on the principle  
13          of using Fe as a catalyst to convert  $H_2S$  to S and  $H_2O$   
14          in a flotation cell. The hydrogen sulfide  
15          containing gas stream in line 9 (Fig. 1) is  
16          continuously fed to a reaction zone in an agitated  
17          flotation cell 37 which contains an aqueous medium  
18          and as a hydrogen sulfide oxidizing catalyst,  
19          chelatic ferric hydroxide dissolved in the aqueous  
20          medium. A separate oxygen-containing gas stream,  
21          usually air is continuously fed through line 38 to  
22          the reaction medium. The process proceeds according  
23          to the reaction:  $H_2S + 1/2 O_2 \rightarrow H_2O + S$ . The sulfur  
24          particles which are formed in the oxidation reaction  
25          are continuously transported to the surface of the  
26          aqueous medium from which the sulfur can easily be  
27          recovered. The sulfur formed is fed back through  
28          line 39 to the heat treatment reactor 4 to enhance  
29          the formation of new dimethyl sulfide or is  
30          withdrawn from the system as crystalline sulfur. If  
31          the gas mixture contained methane, the methane is  
32          separated therefrom and transferred to the lime kiln

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1 through line 31.

2 It should be understood that the preferred  
3 embodiments and examples described are for  
4 illustrative purposes only and are not to be  
5 construed as limiting the scope of the present  
6 invention which is properly delineated only in the  
7 appended claims.  
8

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CLAIMS

What is claimed is:

1. A method of treating black liquor generated in a sulfate pulping process to recover energy and chemicals therefrom, characterized in that

(a) the black liquor is heated at a temperature and for a time period such that substantial volumes of off gases containing organic sulfur compounds are produced;

(b) generating hydrogen sulfide from the off gases; and

(c) utilizing the generated hydrogen sulfide in the sulfate pulping process.

2. The method in accordance with claim 1, further characterized in that in step (b) hydrogen sulfide and methane are generated.

3. The method in accordance with claim 1 or 2, further characterized in that step (c) is practiced by bringing the generated hydrogen sulfide into contact with white liquor, and then using the white liquor in the sulfate pulping process.

4. The method in accordance with claim 1 or 2, characterized by the further step of converting some of the hydrogen sulfide from step (b) into elementary sulfur.



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1                   5. The method in accordance with claim  
2                   4, characterized in that the black liquor heating is  
3                   practiced in a heat treatment reactor, and the  
4                   sulfur is fed back to said heat treatment reactor  
5                   vessel to enhance the formation of dimethyl sulfide  
6                   therein.

7  
8                   6. The method according to claim 1,  
9                   further characterized in that the black liquor  
10                  heating is practiced at a temperature of about  
11                  170-350° C, preferably at about 190-290° C, for a  
12                  time period of about 1-60 minutes.

13  
14                  7. The method in accordance with claim  
15                  2, further characterized by the step (d) of  
16                  separating the hydrogen sulfide from the methane.

17  
18                  8. The method according to claim 7  
19                  further characterized in that steps (c) and (d) are  
20                  practiced by passing a mixture of methane and  
21                  hydrogen sulfide into contact with white liquor to  
22                  absorb the hydrogen sulfide into the white liquor to  
23                  selectively control the sulfur content of the white  
24                  liquor, and then using the white liquor in a sulfate  
25                  cooking step.

26  
27                  9. The method according to claim 7  
28                  further characterized in that step (d) is practiced  
29                  by compression and successive partial condensation,  
30                  or by absorbing the hydrogen sulfide in an amino  
31                  absorber.

32

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1                   10. The method according to claim 7,  
2 wherein the pulping process includes a lime  
3 reburning kiln; and the methane from step (d) is  
4 utilized as fuel in the lime reburning kiln.  
5

6                   11. The method according to claim 2,  
7 characterized in that step (b) is practiced in a  
8 hydroconverter.  
9

10                  12. Apparatus for utilizing black liquor  
11 from a sulfate pulping process comprising:

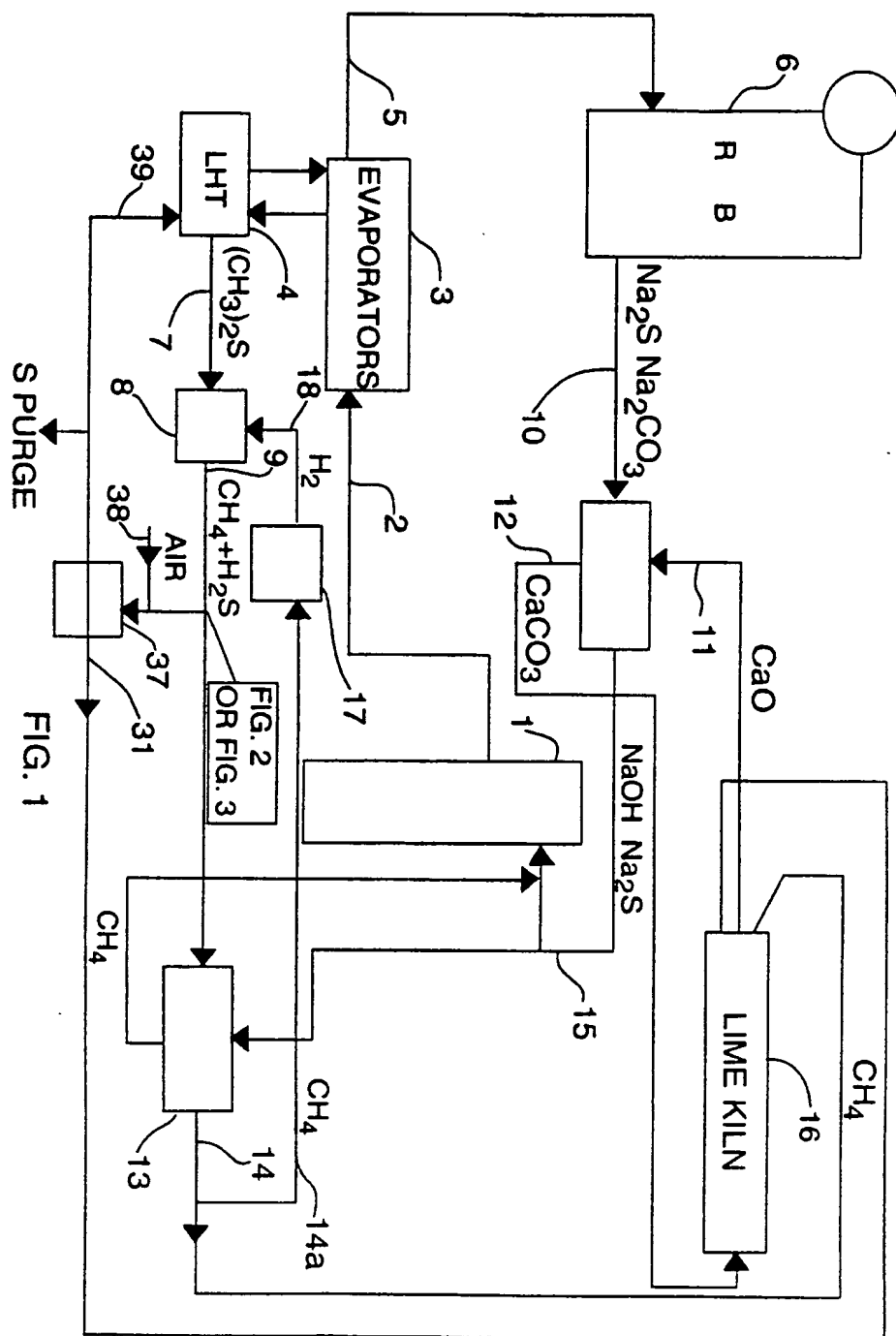
12                   means for heating the black liquor for a  
13 period of time so as to generate off gases  
14 containing organic sulfur compounds;

15                   means connected to the heating means for  
16 generating hydrogen sulfide from the organic sulfur  
17 compounds contained in the off gases;

18                   means connected to the hydrogen sulfide  
19 generating means for controlling the sulfidity of  
20 white liquor and for separating the methane from the  
21 hydrogen sulfide by selectively passing the methane  
22 and hydrogen sulfide into contact with the white  
23 liquor; and

24                   means connected to the sulfidity control  
25 means for feeding the white liquor of controlled  
26 sulfidity to the cooking stage of a sulfate pulping  
27 process.

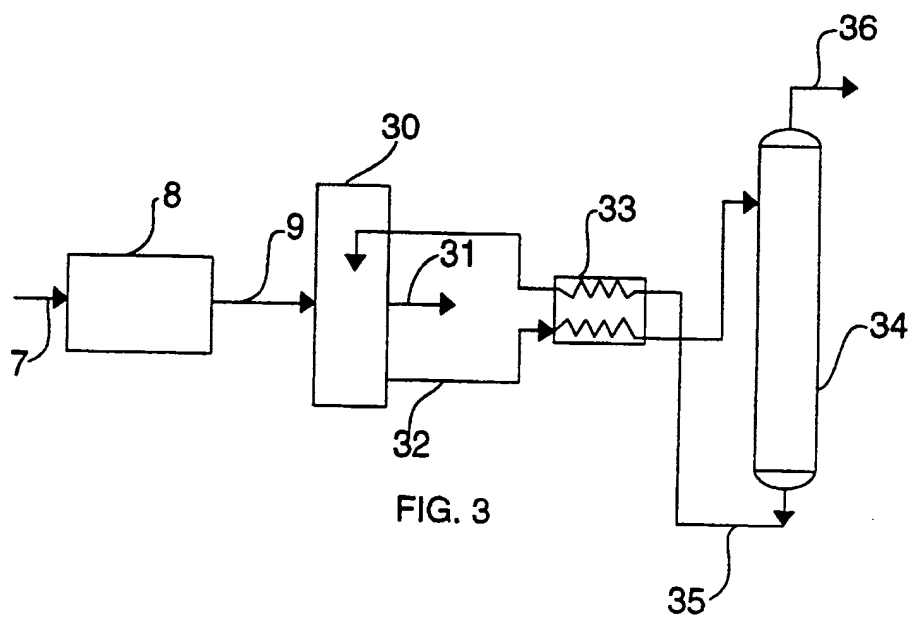
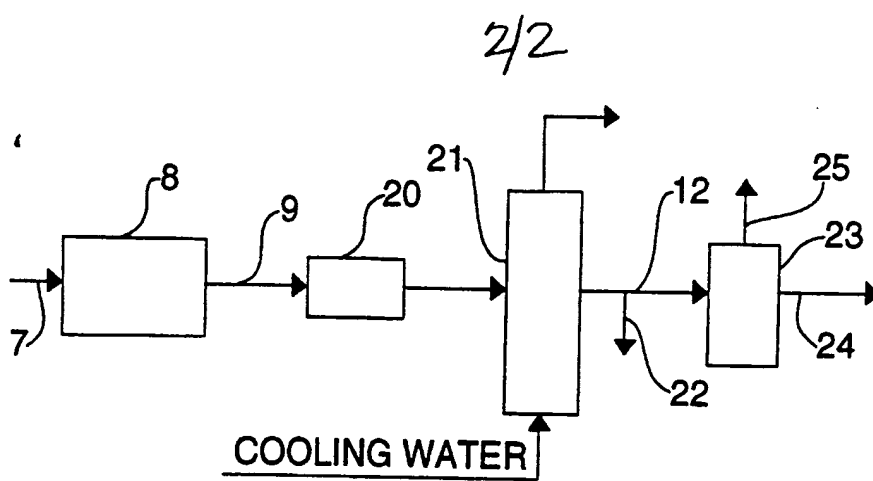
1/2



S PURGE

FIG. 1

SUBSTITUTE SHEET



# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/07021

<b>I. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC(5): D21C 11/00, 11/06, 11/14 U.S. CL.: 162/30.11; 423/207,563, DIGEST 3		
<b>FIELDS SEARCHED</b>		
U.S. 423/206R, 207,228,563, DIGEST 3; 162/30.1, 30.11, 31, 34; 208/209; 585/733		
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched		
<b>II. DOCUMENTS CONSIDERED TO BE RELEVANT*</b>		
Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.?
X	US, A, 3,762,989 (TIMPE) 02 October 1973, See column 3, lines 15; column 6 line 45, column 9, lines 40-60	1-12
A	US, A, 3,718,446 (BRINK ET AL.) 27 February 1973.	4,7,9
A	US, A, 3,607,619 (HESS ET AL.) 21 September 1971, See column 2, lines 65-75.	1-12
Y	US, A, 4,431,617 (FARIN) 14 February 1984, See claim 1.	3,8
A	US, A, 3,944,462 (HESS ET AL.) 16 March 1976.	1-12
A	US, A, 4,851,600 (LOUW) 25 July 1990.	1-12
<p>* Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
23 JUNE 1992		14 JUL 1992
International Searching Authority		Signature of Authorized Officer
ISA/US		GARY P. STRAUB
		REGULATORY DIVISION

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 4,373,109 (OLAH) 08 February 1983.	1-12
A	US, A, 4,513,164 (OLAH) 23 April 1985.	1-12
A	US, A, 4,929,307 (KIISHILA ET AL.) 29 May 1990.	1-12
A	US, A, 4,953,607 (ERKKI ET AL.) 04 September 1990.	1-12
A	US, A, 4,919,914 (SMITH ET AL.) 24 April 1990.	4,7

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_ because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claim numbers \_\_\_\_\_ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out (3), specifically:
  
3. ☐ Claim numbers \_\_\_\_\_ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

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